Cr(VI) Inhibition of Oxygen Reduction on Copper

Martin W. Kendig and Samuel Jeanjaquet
Rockwell Science Center LLC
1049 Camino dos Rios
Thousand Oaks, California 91361

Introduction

Electrolytic reduction of oxygen on intermetallics and redeposited metallic Cu on surfaces of Cu-rich Al alloys appears to play a decisive role in the corrosion of these materials in neutral aqueous solution (1-4). The Cu cathodes originate from the intermetallic phase (5) as well as the matrix(4).

Aqueous hexavalent chromium species inhibit corrosion of these alloys. Even retained hexavalent chromium released from chromate conversion coatings have been shown to increase the corrosion resistance of Al 2024-T3 by several orders of magnitude (6).

There is strong evidence that Cr(VI) inhibits corrosion of these materials by inhibiting oxygen reduction on the highly dispersed cathodes present on the alloy surface. One hypothesis states that the Cr(VI) migrates to the cathodically active sites where it irreversbily reduces to form a protective Cr(III) oxide film that subsequently blocks the cathodic reduction of oxygen. Others, however, raise the possibility that the cathodic reduction of aqueous Cr(VI) species is not necessary for inhibition.

Questions involving the relative role of Cr(III) and Cr(VI) in the inhibition of oxygen reduction on Cu and the ability of non-chromate inhibitors to limit oxygen reduction on Cu motivates this work. Development of a rapid test for screening oxygen reduction inhibitors provides further motivation. Results to be presented provide illustrate the role of Cr(VI) and other prospective inhibitors in influencing reactions on Cu cathodes.

Summary of Experimental Results

All experiments were performed in a nominal pH 6 5% NaCl electrolyte with and without the addition of a chromate/dichromate buffer made up in the same 5% NaCl. Experiments were performed on a 1 mm diameter stationary Cu disc electrode with a 600 grit finish or a Cu 1 cm diameter rotating disc electrode (RDE). All potentials are expressed vs. SCE

Figure 1 shows the currents that result from polarization of a stationary Cu electrode in the electrolyte with varying quantities of Cr(VI) and Ce(III) species or atmospheric oxygen. The Cr(VI) inhibits the oxygen reduction reaction in the –0.6 to –0.8 V region but is reduced in the –0.8 to –1.0 V region as indicated by the concentration dependent limiting current densities. This suggests that Cr(VI) inhibits oxygen reduction. Ce(III) cations appear to have no inhibiting influence in the –0.6 V to –0.8 V region where Cr(VI) lowers reduction currents.

Figure 2 shows the diffusion limited currents obtained for a Cu RDE biased at –0.7 V as a function of the reciprocal diffusion layer thickness, δ^{-1}, where $\delta = 1.75\omega^{-1/2}\nu^{-1/6}D.^{1/2}$ The current depends on the hydrodynamically defined diffusion length in the absence of any inhibitor. Addition of 0.01 M Cr(VI) virtually eliminates rotation rate dependence and lowers the current. A 100-fold difference between the Cr(VI) inhibited and inhibitor free currents requires as determined by extrapolation (Figure 2) a δ of 2.6 μm, a scale typical for the cathodes on Al 2024 T3 in 5% NaCl.

Summary

The following points appear from this work: (1) Cr(VI) can inhibit oxygen reduction on Cu. (2) The presence of small quantities of Cr(VI) (0.01 M) inhibits oxygen reduction on Cu. (3) If inhibition of oxygen reduction on cathodes on Al 2024-T3 by chromate is the only mechanism of inhibition by chromate, then a reduction in corrosion rate by 2 orders of magnitude implies that the scale of cathodes on the alloy is between 2-3 μm. (4) Ce(III) at the same concentration levels as Cr(VI) appears to have no inhibiting effect on oxygen reduction.

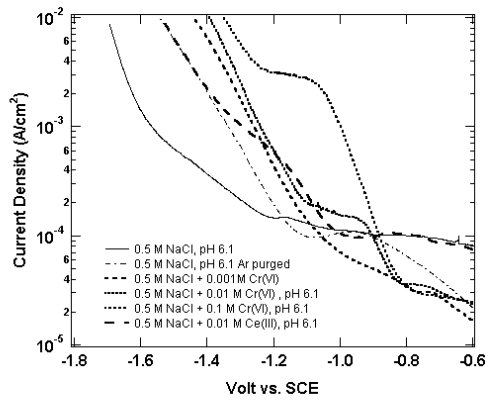

Figure 1. Polarization curves for Cu in 0. 5 M NaCl.

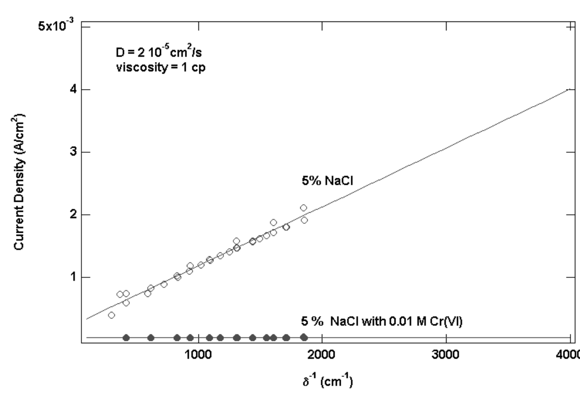

Figure 2. Current density on a copper RDE biased to –0.7 V in 5% NaCl.

References

1. J. R. Scully, T. O. Knight, R. G. Buchheit, E. E. Peebles, Corros Sci 35, 185 (1993).
2. R.G. Buchheit, R.P. Grant, P.F. Hlava, B. McKenzie, G.L. Zender, J. Electrochem. Soc., 144, 2621 (1997).
3. V. Guillaumin and G. Mankowski, Corr. Sci., 41, 421 (1999).
4. N. Dimitrov, J. Mann, K. Sieradzki, J. Electrochem. Soc. 146(1), 98 (1999)
5. R. Buchheit, M. A. Martinez and L. P. Montes, J. Electrochem. Soc, 147:(1) 119-124 (2000).
6. J. Zhao, G. Frankel, R. McCreery,J. Electrochem.Soc.,145(7), 2258 (1998).

Ackowledgement

This work was supported by the Air Force Office of Scientific Research under contract # F49620-96-1-0479.